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STUDY OF AGGREGATION BEHAVIOR AND ELECTRON INJECTION PROCESS OF THIOL SUBSTITUTED Zn-PHTHALOCYANINE DERIVATIVE ON TiO_2 NANOPARTICLE SURFACE

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ABSTRACT

Tetra carboxyl Zn-phthalocyanine (TCTZnPc) with thiol linker is anchored onto titanium dioxide (TiO_2) nanoparticles surface. The presence of a thiol group having lone pair of electrons further increase the electron donating capability of Zn-Phthalocyanine (ZnPc) derivative. TiO_2 thin film is prepared and sensitized with the Zn-Phthalocyanine derivative. The type of aggregation of TCTZnPc in DMF and on TiO_2 surface is studied from the steady-state absorption spectral techniques. The fluorescence spectral studies are carried out to analyze the quenching of ZnPc fluorescence on TiO_2 surface. Further, the time-resolved fluorescence is carried out to confirm the electron injected from excited state TCTZnPc to the TiO_2 nanoparticles conduction band.

Keywords: ZnPc, Aggregation, TiO_2, Q-band, Electron injection

INTRODUCTION

Phthalocyanine (Pc) is an 18 π-electron conjugated macrocyclic system which tantalize great interest because of their manifold applications ranging from the medical field to materials chemistry. Numerous modifications were done in the macrocyclic molecule either by introducing different central metal ions or by substituting various functional groups at peripheral positions of phthalocyanine (Pc) ring.[1,2] The peripheral (β) substitution of functional groups in the ZnPc ring is supposed to increase the solubility of phthalocyanines in various organic solvents and alters the electronic spectrum depending on their properties.[3] Zinc phthalocyanine (ZnPc) complexes have aroused much interest, due to their considerably higher triplet state quantum yield and longer triplet lifetime[4]. Being a versatile group of functional dyes, phthalocyanines possess fascinating and tunable photophysical, catalytic, optoelectronic and self-assembly properties.[3] Moreover, at present researchers emphasis phthalocyanines based research especially as dyes and its potential applications.[3,4]

In the past few years, the concentration of research on Pcs has been pivoted on applications in material science.[5-7] The phthalocyanines have characteristic strong absorption in Q-band region (~690 nm), as

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well as promising electro-chemical properties, photo-chemical properties and thermal properties, and also applicable as near IR photosensitizer in the fabrication of the dye-sensitized solar cells (DSSCs). For the above-mentioned purpose, a wide range of phthalocyanine derivatives have been synthesized for the applications in DSSCs.[8] Upon absorption of light, an electron from the excited singlet state of the photosensitizer (LUMO) is injected into TiO_2 nanoparticle film (mesoporous TiO_2) conduction band.[9,10] The rate of the forward electron transfer process is ultrafast in the scale of 100 fs to 10 ps. The Zn-phthalocyanine molecules have been investigated extensively by various research groups.[11,12] Aggregation is characterized by the Q-band absorption of phthalocyanine, which shows a red or blue-shift relative to monomer, depending on the different molecular interactions.[13]

In general, the H-aggregates represent the blue-shifted absorption, whereas the uncommon class of aggregation called J-aggregates represents a red shift in the absorption. The photo-induced charge separation yield at the dye/nanoparticle interface is limited by aggregation of adsorbed organic dye on the TiO_2 nanoparticles. The changes in adsorption geometry of adsorbed dye molecules and/or molecular energy levels due to the aggregation, leads to the lower power conversion efficiency.[14] It is well established that the phthalocyanine dyes exhibit strong aggregation and this restricts the application of those dyes and its derivatives in DSSCs, although they exhibit a strong near IR absorption, and chemical and thermal stability.[15,16] The phthalocyanine tends to form strong aggregation in solution and on films, which in turn to limits the excited state lifetime and device efficiency.[17,18,19] Thorough investigation of aggregation tendency of Phthalocyanines (Pcs) on semi-conductor surface is necessary to understand and design an efficient photosensitizer for application in DSSC.

In the present work, the aggregation tendency of Zn-phthalocyanine in dimethyl formamide (DMF) and on TiO_2 nanoparticles surface is investigated. The aggregation of ZnPc is observed in the DMF and on TiO_2 surface. However, H-aggregation is enhanced on TiO_2 surface than in solution. In addition to H-aggregation, J-aggregation is also observed on the TiO_2 surface. The complete fluorescence quenching of ZnPc on TiO_2 surface indicates the electron injected from the excited state of Pcs dye molecule to the TiO_2 conduction band.

EXPERIMENTAL

Solvents used in this study were acquired from the Fischer Scientific and are used as such without further purifications, the materials used in the synthesis are acquired from Sisco Research Lab and Aldrich. For the spectral studies, HPLC grade solvents were used. Titanium dioxide paste (Ti-nanoxide HT/SC series) is purchased from Solaronix.

TiO_2 Film Preparation and Dye Coating

The synthesis, characterization and photophysics of TCTZnPc derivative are already reported by our group.[14] TCTZnPc dye coated nanocrystalline TiO_2 film was prepared by following the procedure as reported earlier.[15]

Experimental Setup

Complete details of the list of instruments used in the present study are reported earlier.[16]

Quantum Yield Measurements

Measurement of fluorescence quantum yield was done by employing the methods as reported earlier by our group.[16]

RESULTS AND DISCUSSION

Absorption Spectral Studies

Fig.1 shows the absorption spectrum of TetraCarboxylThiol Zn-Phthalocyanine (TCTZnPc) in solution (DMF). From the spectrum, it is observed that the strong bands located at 352nm, 640nm and 684nm. The absorbance at 352nm, is assigned to the S-band absorption originated from to π-π^* transition. Broad absorption band around 640 nm tends to the ability of the TCTZnPc to form H-aggregation in DMF. Moreover, a sharp Q-band absorption appears at 684 nm corresponds to π-π^* transition, which indicates the lack of J aggregates in DMF solvent. In general, Phthalocyanines exhibits a higher tendency to aggregate in nonpolar solvents, whereas they exist mainly as a monomer in polar solvents.[20,3] However, the H aggregation of TCTZnPc is noted even in a polar solvent such as dimethyl formamide (DMF) in the present investigation. It demonstrates that TCTZnPc possesses the tendency to form stacking, irrespective of the solvent polarity. The shoulder bands located at 610 and 640 nm, which are ascribed to vibrational progression is not observed due to a higher extent of H-aggregation.

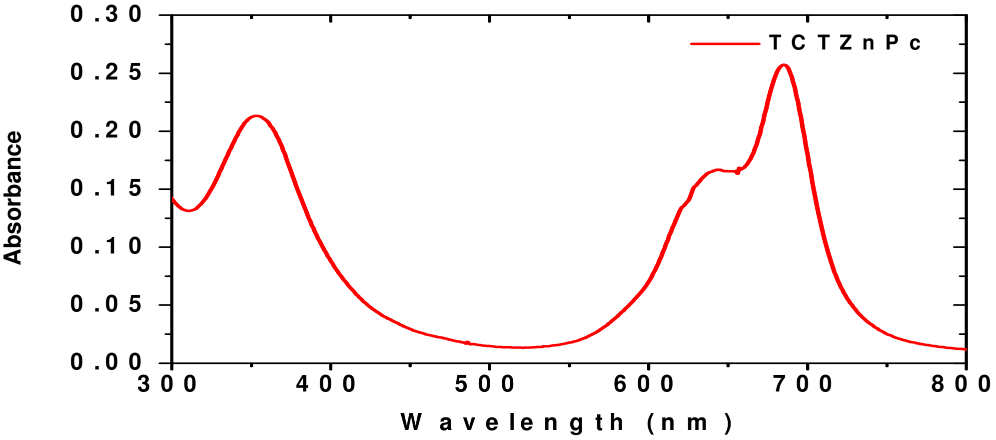

Fig.-1: Absorption Spectrum of TCT ZnPc in DMF Solvent.

The absorption spectrum of TCTZnPc on TiO_2 surface (Fig.-2a) is shown the TiO_2 band edge absorption, H-aggregation 640 nm and Q-band absorption at 690 nm.[20,21] The 6 nm red shift of Q-band absorption is ascribed to the formation of J-aggregate on TiO_2 surface.[22] The peak height at 640 nm and 690 nm are similar, which indicates the higher extent of H-aggregation on TiO_2 surface than in DMF. From the normalized (Fig.-2b) absorption spectra of TCTZnPc in DMF and on TiO_2 surface, shows the proportion of H-aggregation of TCTZnPc on TiO_2 surface is higher than in DMF. In addition to the higher proportion of H-aggregate on TiO_2 surface is observed that 6nm red shift of Q band absorption from 684nm to 690nm indicates the J-aggregation of TCTZnPc on TiO_2 surface. The presence of TiO_2 band edge absorption for TCTZnPc/TiO_2 is showed the adsorption of TCTZnPc on TiO_2 surface. The presence of –COOH group facilitates the covalent linking of ZnPc on TiO_2 surface.

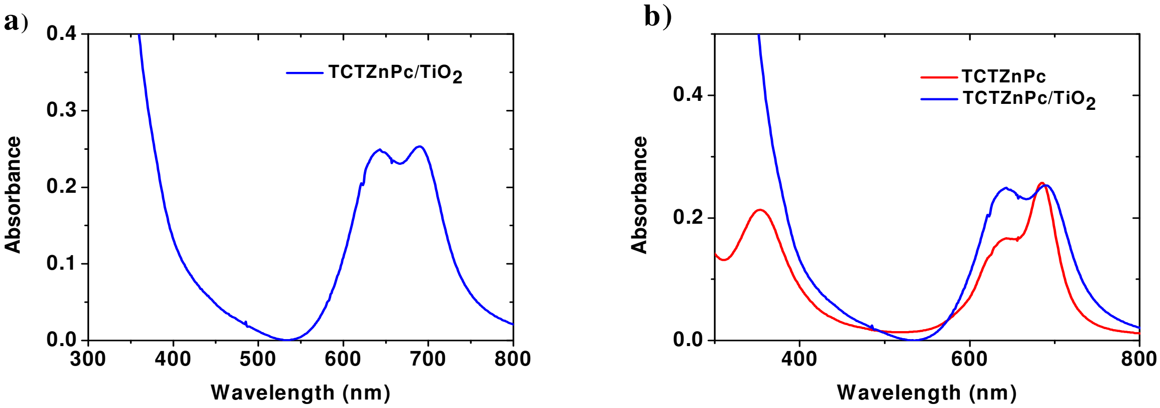

Fig.-2: Absorption Spectrum of (a) TCTZnPc on TiO_2 Film, (b) Normalized Absorption Spectrum of TCTZnPc in DMF (Red Line) and on TiO_2 Film (Blue Line).

Fluorescence Spectral Studies

From fig.3 the emission spectrum of TCTZnPc in DMF solvent shows maximum at 693nm. The fluorescence (QY) quantum yield value is found as 0.14. In general, the fluorescence spectrum of ZnPc shows a nearly exact mirror image of the absorption spectrum including the vibrational progression. However, it is not observed for TCTZnPc due to aggregation which indicates the broad absorption band around 640 nm is assigned to aggregation and not due to vibrational transition. The complete fluorescence quenching is observed for TCTZnPc on TiO_2 surface.

In general, ZnPc with thiol group acts as the strong electron donor and semiconductor nanoparticles such as TiO_2 and Zinc oxide (ZnO) is exhibited as a strong electron acceptor. From the results, it is cleared that, an electron injected from TCTZnPc to TiO_2 surface. The electron transfer occurs from the excited singlet state of the ZnPc results in fluorescence quenching. The electron transfer process is further confirmed from time-resolved fluorescence studies. In general, J-aggregation enhanced the fluorescence. From the results, it is concluded that the quenching of emission is attributed to the electron injected from TCTZnPc to TiO_2 surface and not due to aggregation on the nanoparticle surface.

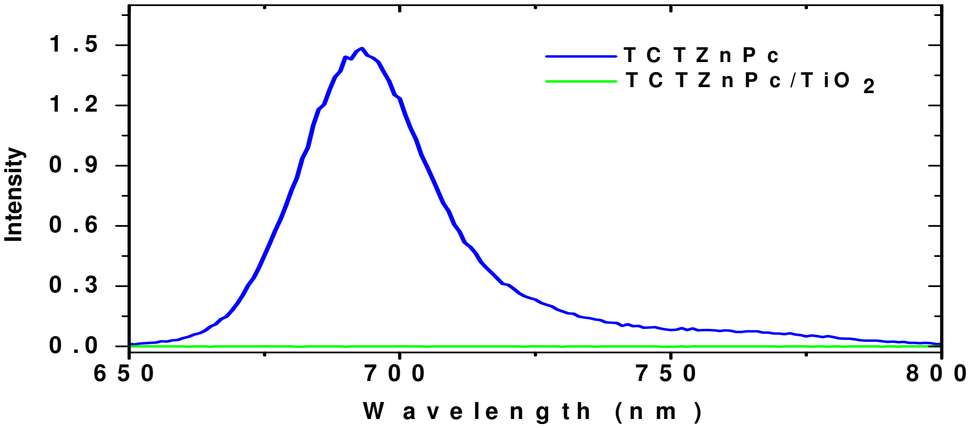

Fig.-3: Fluorescence Spectrum of TCTZnPc in DMF (Blue Line) and on TiO_2 Film (Green Line).

Time-Resolved Fluorescence Studies

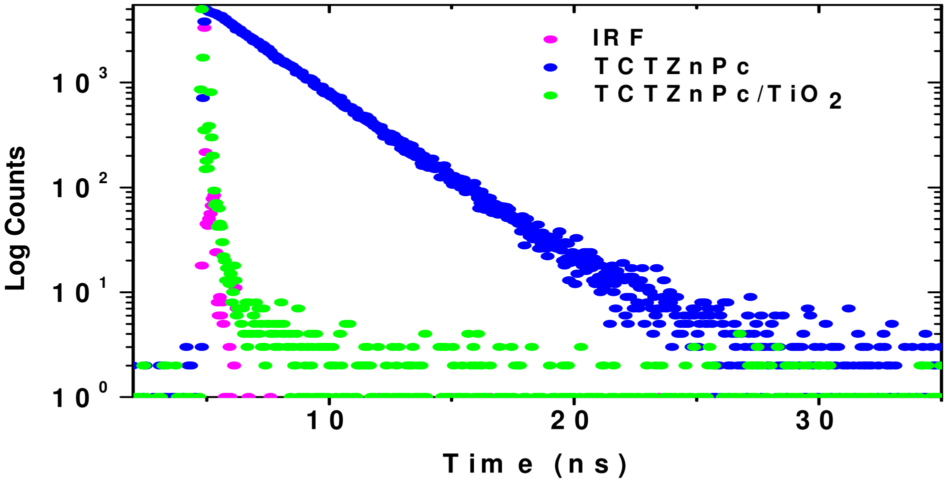

Fig.-4: Time-resolved Fluorescence Decay of TCTZnPc in DMF (Blue Circles) and on TiO_2 Film (Green Circles).

The time-resolved fluorescence decay for TCTZnPc molecule in DMF solvent (Fig.-4) fits in single exponential with a lifetime of 2.7ns, which is assigned to relaxation from singlet excited state to ground state. The fluorescence decay of TCTZnPc on TiO_2 surface is showed the complete fluorescence quenching. The complete fluorescence quenching of TCTZnPc is ascribed to electron transfer from TCTZnPc to TiO_2 surface. Thiol group present in the dye molecule is also assisted for the efficient electron injection process.

Transient Absorption Spectral Studies

The transient absorption study was done by exciting the phthalocyanine molecule at 355nm and recorded the transient absorption spectrum in the range 400nm to 800nm. Transient absorption of TCTZnPc shows, a broad absorption from 400nm to 600nm, with a maximum at 500nm (Fig.-5), which is ascribed to the triplet-triplet absorption and the bleaching at 690nm corresponds to the ground state (S_0) absorption of TCTZnPc in DMF. Whenever the electron transfer takes place from the excited state dye molecule to the conduction band of semiconductor nanoparticle, thereafter, a cation radical of TCTZnPc is formed. The TA spectra (Fig.-5) of TCTZnPc on TiO_2 film shows maximum at 520nm, which is 20nm red-shifted from the transient absorption maximum of TCTZnPc alone in DMF solvent. The maximum at 520nm was ascribed to the cation radical of the ZnPc.[23] This confirms the electron transfer from the TCTZnPc excited state to the TiO_2 nanoparticle conduction band.

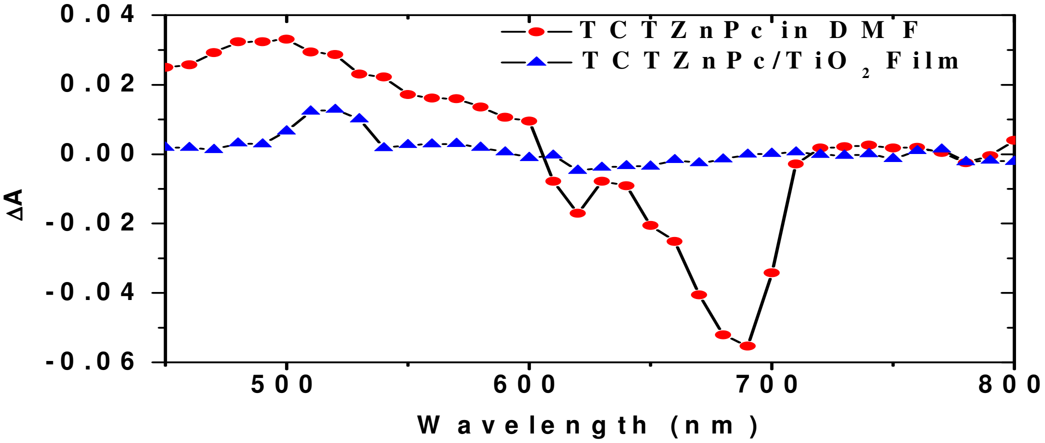

Fig.-5: Triplet-triplet Absorption Spectra of TCTZnPc in DMF (Red Circles) and on TiO_2 Film (Blue Triangle).

CONCLUSION

In this work, the photophysics of TCTZnPc in DMF (solution) and on TiO_2 surface (film) are investigated. The absorption spectral study reveals, TCTZnPc formed the H-aggregate in DMF and both types - H and J-aggregates on TiO_2 surface. From the fluorescence spectral studies, the complete fluorescence quenching of TCTZnPc on TiO_2 surface is observed, which can be attributed to the electron injection from TCTZnPc to TiO_2 surface and not due to aggregation on the nanoparticle surface. Further, it is confirmed from the fluorescence lifetime studies. Electron transfer from TCTZnPc to TiO_2 nanoparticle is observed from transient absorption spectral studies. The study establishes that the ZnPc molecules aggregate in solution and on TiO_2 surface and assist for designing the perfect non-aggregated ZnPc for various applications.

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